Incommensurate systems as a model approach to low temperature behaviour of glasses

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Abstract

The Debye model predicts a T^3 dependence of the specific heat C_p at *sufficiently low* temperatures in insulators and it reproduces a wealth of data in isotropic crystals. However, this simple and general law fails to account for the low temperature specific heat of amorphous compounds and this matter is currently the focus of many scientific activities, yet unsettled. At low temperatures there are two anomalies that show up as an excess to the constant $C_p(T)/T^3$ in glasses and amorphous systems: the upturn below 1 K and a broad bump at T≈10 K named Boson peak (BP). Whereas insulating crystals with low-lying optical modes and/or acoustic modes with non-linear dispersions can exhibit a similar bump in the specific heat, the Debye law is expected to re-emerge in these systems at sufficiently low temperatures. (Andres) One question that we want to address is to what extent this is the case. We show that, contrary to the expected, the Debye law is not fully obeyed as soon as translational periodicity is slightly broken like in insulating crystals with incommensurate superstructures. (Our suggestion) We show that, however, as soon as translational periodicity is slightly broken, like in insulating crystals with incommensurate superstructures, the Debye law is not the most important contribution to the low temperature specific heat anymore. On general grounds we show the specific heat of incommensurate modulated systems bears many similarities with that of amorphous systems. Moreover we account for the excess of heat capacity within a simple model in which the energy dispersion and the damping of the lowest energy, non-acoustic, phonon branch are the main parameters.

Keywords: Incommensurate systems, thermodynamics, vibrational states, low-energy excitations, glasses, Boson peak

Incommensurate crystals lack the translational periodicity, while retaining the structural order. In their simplest presentation of a zero-dimensional (0D) modulation the diffraction pattern is given by a single modulation wavevector expressed as an irrational combination of at least one of the three basic reciprocal lattice vectors that represents the average lattice (see Figures 1a and 1b). Non-linear forces, anharmonicity, are at the very basis of the IC phase transitions. The same anharmonicity is responsible for the occurrence of discommensurations (or phase jumps giving rise to some kind of phase disorder) in the ground state of the modulation.

IC structures emerging in a displacive phase transition that is, a phase transition associated to a soft phonon mode, see Figure 1c) display a specific dynamics with the occurrence of two distinct excitations in the close neighbourhood of the modulation wavevector: the low energy phason mode and gapped amplitudon mode (see Figure 1d). They arise from the even and odd combination of the original soft phonon mode coordinates, respectively. Although this decoupling is mathematically exact in the pure displacive limit of the phase transition, extensions to phase transitions including both soft mode and relaxation dynamics can also be made. Important for low temperature heat transport is the possibility that the phase mode is gapped (Figures 1b and 1c), and thus contributing to the specific heat as a deviation from the T^3 law [1]. A second feature that is acknowledged to be present in many (if not all of) compounds is that the phason mode is damped [2] (Figure 1e), or even over-damped as in K_2SeO_4 [3]. At this point, and for the sake of completeness, it is important to recall that many IC compounds do not have a soft mode, the pretransitional dynamics are rather of the relaxational type. In this case the decoupling soft phonon $\rightarrow$ phason+amplitudon is not observed in the inelastic neutron scattering (INS) spectra. However, the lowest energy soft mode of the correct symmetry acts as both the phason and the amplitudon and consequently the low temperature specific heat still bears similar features as those here described [4, 5].

One of the best known examples of phonon softening is the Kohn anomaly due to electron-phonon coupling and the Fermi surface instability of 1D electron subsystem at the wavevector $q_{IC}=2k_F$. This is the Peierls mechanism for metal insulator phase transition. In this case, the $2k_F$ instability gives rise to an incommensurate (IC) charge density wave

FIG. 1. Overall sketch of the displacive dynamics in incommensurate compounds. (a) 2D picture of the reciprocal space for T>T_C with the Bragg peaks in red. (b) Idem for T<T_C, and the blue dots are the new peaks (or satellite peaks) originating from the IC phase transition. (c) Phonon softening above the transition temperature at an incommensurate position, namely q=0.31. (d) Decoupling of the phonon coordinate into an amplitudon and phason modes. The amplitudon frequency renormalizes very strongly at low temperatures. (e) The phason branch in gapped, with value Δ, and damping, Γ.

(CDW) and the concomitant lattice distortion that stabilizes the electronic phenomena [6–8]. The bump in C_p/T^3 in CDW systems such as $NbSe_3$, TaS_3, $(TaSe_4)_2I$, $K_{0.3}MoO_3$ was described as the contribution from the modified Debye spectrum with two cut-offs: a lower frequency corresponding to the pinned CDW state and an upper frequency corresponding to the effective Debye temperature for the collective modes (modified Boriack-Overhauser model) [1, 9]. As shown in Figure 2, the bump is accompanied at low temperatures by an extra contribution scaling roughly as T^{-2} in the C_p/T^3 plot. As in glasses it has been explained by invoking the presence of TLS and described as the tail of the corresponding Schottky anomaly. These metastable states, found also sensitive to the magnetic field [10], are attributed to the bisolitons generated at strong pinning centers in the CDW ground state[11, 12]. They are decoupled from phonon modes, so that the specific heat exhibits non exponential relaxation with aging effects [13]. Surprisingly these two features bare many similarities with identical plots in glasses. In the upper middle panel of Fig. 2 we show the specific heat of vitreous silica [14] for comparizon.

In addition, a wealth of experimental evidence has been collected indicating that the CDW also forms a kind of charge density glass (CDG) at low temperatures [15, 16]. The similarity of the phenomenology of CDW systems and other electronic crystals suggests that the low-T glass state is a universal feature in modulated electronic superstructures. Interestingly enough, what makes the CDW state dynamics unique among IC compounds is that the CDW-phase fluctuations (or phasons) induce changes in the electron density which are coupled by long-range Coulomb interactions. Early theories soon recognized that at T=0 K the effect of such interactions is to transform the acoustic-like longitudinal phason mode

FIG. 2. $C_P/\beta T^3$ plots of several IC compounds, with β the coefficient of the Debye law. Left and middle panels are charge density wave compounds ($K_{0.3}MoO_3$ [9], $(TaSe_4)_2I$ [20], KCP [9] and TaS_3 [16]). $C_P/\beta T^3$ plot of vitreous silica is displayed as a comparison [14]. Right panel, insulating compounds, BCPS ($(ClC_6D_4)_2SO_2$) [21] and biphenyl [22]

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FIG. 3. Temperature dependence of the specific heat divided by T^3 in a log-log plot for $ThBr_4$. Experimental data are displayed with full black circles. The black line represents the Debye contribution calculated from sound velocities determined in neutron scattering experiment [23] and using the Debye model of the dispersion with $\theta_D \approx$62 K and corresponding β=8$\cdot$10^{-3}J/mole K^4. The green line is the amplitudon contribution estimated from the measured INS dispersion. Full red circles represent the contribution remaining after subtraction of previous contributions, and assigned to the phason contribution.

into an optical one [17]. At finite temperatures however, the quasiparticles excited across the CDW gap screen out the Coulomb interactions and bring back the acoustic character of the phason [18, 19].

In order to elucidate the key ingredient that induces a glassy dynamics in IC systems, we have extended our investigation to the case of modulated IC dielectrics for which the incommensurability is of a purely structural origin (and therefore electronic contributions, as in CDWs, are absent). A gapless phason is expected for an ideal, defect-free structure remaining incommensurate down to the lowest temperature. The work on dielectrics was initiated some years ago on $(ClC_6D_4)_2SO_2$ (BCPS) [21] and byphenil [22] that show also a deviation from the Debye behavior at low temperatures, as it is shown in Figure 2, and associated to the phason and amplitudon modes of the IC structure. An excess in the phonon density of states was observed as well, but a proper quantification of the anomalies is still lacking. Figure 2 illustrates at its best the fact that, as in glasses and amorphous systems, the Debye law approximation does not hold in IC compounds at low temperatures. As we will show below the presence of excitations related to the breaking of translational periodicity is a more fundamental feature that determines the specific heat at low temperatures.

A proper account of the specific heat at low temperature calls for a quantification of the low energy excitations, phonons and the modes originating from the IC structure. Here we present the investigation of the low temperature specific heat of $ThBr_4$. This system is an insulator that undergoes a displacive-like transition to the 1**q**-IC modulated superstructure at 95 K, with T-independent (between 80 K and 1.5 K) wave vector $\mathbf{q}_{IC} = 0.31\mathbf{c}^*$. This phase transition has been very well documented in the literature [23] and it is considered as one of the clearest examples of displacive dynamics and of the presence of phason and amplitudon excitations below the transition temperature. Interestingly the phase-mode dispersion has been measured along different directions[23] and therefore its contribution to the specific heat can be computed and straightforwardly compared with experiments.

The results of the specific heat measurements in $ThBr_4$ are shown in Figure 3 which can be decomposed as follows: *(i)* The background constant contribution in the $C_p(T)/T^3$ plot due to acoustic phonons. The Debye temperature θ_D =62 K has been calculated from the sound velocities measured by INS [23], yielding $\beta = 8 \cdot 10^{-3}$ J/moleK^4 (see Supplementary Material). *(ii)* As in previous works the amplitudon contribution, as revealed by the bump in the $C_p(T)/T^3$ plot, lies at around 10K. This contribution was estimated from the amplitudon dispersion with a gap of 570 GHz determined by Raman scattering measurements at low temperature [24] (see Supplementary Material). Red points in Figure 3 represent the specific heat after subtraction of these two contributions. It can be described as a bump followed by a rise as the temperature decreases. These features have been regularly considered in the literature as separated and having uncorrelated origins: the shoulder as mostly due to the phase gap and dispersion while the low temperature rise corresponding to the tail of a Schottky anomaly, originating from the presence of TLS as in glasses.

Cano and Levanyuk have proposed a plausible explanation for these striking features in insulating crystals [25]. In this picture, both the shoulder (that appears between 1 and 0.5 K in Figures 3 and 4) and the subsequent rise can be described within the same formalism revealing that they are two different manifestations of the very same phason mode: gap and damping. The shoulder indicates that the phason dispersion in $ThBr_4$ is not completely acoustic-like as in textbook descriptions, but contains a low-frequency gap (the phason dispersion is shown as an inset of Fig. 4). This is not very surprising since,

FIG. 4. Low energy contribution to the specific heat of $ThBr_4$ divided by T^3 in a semi-log plot. The red points correspond to the experimental data shown in Fig. 3 once the Debye and amplitudon contributions have been subtracted. The continuous black line is the result of the calculation from Eq. (1) in Supplementary Materials with the phason gap of 46 GHz and damping of 3.8 GHz. The black dash lines correspond to simulations using the same damping and different phason gaps of 20 and 90 GHz. Dispersion curve for the phason is drawn in the inset, with points representing the experimental data.

physically, the incommensurate superstructure is expected to be pinned to the underlying lattice rather than detached from it and totally free to move at no energy cost. According to Ref. 23, the upper limit of this gap can be estimated as $\approx$ 50 GHz. In addition, it was pointed out that the finite life-time of the phason excitations can play a non-trivial role in the low temperature properties of incommensurate systems. Such a finite life-time has been experimentally observed by INS [26] within the temperature range of our specific heat data. This lifetime again evidences that the incommensurate superstructure cannot propagate freely. It will also be subjected to dissipation, which can be due to the scattering with impurities and/or disorder. This dissipation amounts to a redistribution of density of states that, as a rule, is ignored when addressing thermodynamic properties. However, and as pointed in Ref. 25, this redistribution cannot be neglected in incommensurate systems given the low-frequency of their characteristic phason modes, which can be the reason of their systematic low-temperature anomalies.

Figure 4 displays the results of a fit of the low temperature specific heat of $ThBr_4$ below 10 K, following Eq. 1 in the Supplementary Material section. Parameters extracted from the fits are phason gap of 46 GHz and phason damping of 3.8 GHz. The fit nicely reproduces the experimental behavior. We emphasize that the key ingredients are just the phason dispersion and the corresponding lifetime, which corresponds to those obtained in previous inelastic scattering experiments (independent from our measurements). Black curves in Fig. 4 show how the agreement with the INS data is sensitive to the actual value of the phason gap when Δ=22GHz and Δ=90 GHz for the same damping.

We have established that the excess of specific heat at low temperature (or bump in the $C_p(T)/T^3$ plot) in $ThBr_4$ directly originates from gapped phase and amplitude modes of the incommensurate structure. Despite previous work in IC compounds this is the first time that we can quantitatively establish this correspondence beyond reasonable doubt [27]. As previously suggested [25], the two anomalies observed in the low temperature specific heat of $ThBr_4$ and, in general, of all studied incommensurate compounds can be described under the same and unique formalism by taking into account both the phason (or in general a low energy phonon mode of the appropriate symmetry) gap value and its damping. Anharmonic interactions acting at the IC wavevector are thus at the origin of both features.

Summarizing, we have demonstrated the intrinsic limitations of the Debye model for describing the low temperature heat capacity of solids lacking of translational periodicity. For $ThBr_4$, the simplest case of an incommensurate insulator, we have shown that low energy modes associated to the incommensurate superstructure dominate its low temperature heat capacity. This type of incommensurate systems represent the simplest "zero order approximation" of amorphous solids and glasses lacking crystalline order.

Moreover, the concurrence between IC systems and glasses goes beyond a similar specific heat dependence at low temperatures. Incommensurate modulated structures can be conceptually viewed as the simplest approach to the structure (and dynamics) of an amorphous (glass) system. Starting from a crystalline structure, the amorphous state can be pictured as a multiply incommensurate modulation with every q-position being a modulation q-vector. The modulation wavevectors thus span the 3D Fourier space. Conversely an incommensurate system is, in its simplest form, a 0D, just a single q-position, modulated structure. The overly anharmonic interactions present in glasses, and certainly at the origin of the low temperature features in the specific heat data, are present in IC systems as well, in the form of modes such as phason and amplitudon, or more generally under the form of low lying phonon modes. Thus the intrinsic IC compounds low energy dynamics constitute a plausible simplification of the landscape of interactions giving rise to the characteristic low temperature anomalies in glasses. Such a view is compatible with recent molecular dynamics simulations in glasses [28–30], which we expect to make the link between these two seemingly unrelated areas of research.

Materials $ThBr_4$ crystals used in our experiment were the same used in the INS studies [23]. They were synthesized by P. Delamoye and kindly lent by R. Currat. As known to be highly hygroscopic, the sample has been kept in the vacuum-tight Pb container for the last 15 years. In order to avoid any contamination, its further handling for specific heat measurements was done in a glove box under a controlled nitrogen atmosphere. There, the sample of total mass 243 mg, broken in two pieces while removed from the Pb container, was embedded in 38 mg of Apiezon-N grease usually used to improve thermal contact. This grease is a very good protection from air and water contamination during transfer from the glove-box to the cryostat. C_p data were obtained by a transient heat pulse technique[9]. The heat capacity of the addenda was below 30% of the total in the whole T-range, except for T$\geq$ 20 K where it was between 30% and 40%.

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